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LETTER TO THE EDITOR

EFFECT OF COLD WORK ON THE OXIDATION OF IRON IN WATER VAPOUR AT 550°C*

IT IS interesting to learn from Dr. Price[1] that cold work increases the oxidation of Fe in CO_2 below 550°C, similar to our results on Fe in O_2.[2] We have recently observed the same effect at 550°C in water vapour. The parallel behaviour in three oxidizing atmospheres appears to broaden the scope of the proposed mechanism that the cold-worked metal surface provides sinks for the cation vacancies flowing inward to the oxide–metal interface thereby minimizing interfacial detachment.

Figure 1 shows the oxidation curves of annealed and annealed + abraded 99·997% Fe (zone-refined Battelle ultrapure iron) oxidized in water vapour–argon for 20 h at 550°C. The experimental details have been described previously.[2] Included for comparison is a similar abraded–annealed pair oxidized in dry O_2 for 20 h at 550°C. With both preparations oxidation is much greater in O_2 but in each atmosphere cold-worked Fe oxidizes more rapidly than annealed Fe. The apparent parabolic rate constants are 11×10^{-11} and $0{\cdot}98 \times 10^{-11}$ $g^2\ cm^{-4}\ s^{-1}$ for the abraded and annealed Fe respectively in O_2. In water vapour–argon the corresponding initial apparent parabolic rate constants are $3{\cdot}0 \times 10^{-12}$ and $0{\cdot}55 \times 10^{-12}$ $g^2\ cm^{-4}\ s^{-1}$ for abraded and annealed Fe respectively; however, after 4 h the curves become straight lines with linear rate constants $8{\cdot}8 \times 10^{-9}$ (abraded) and $2{\cdot}4 \times 10^{-9}$ $g\ cm^{-2}\ s^{-1}$ (annealed). Because of structural abnormalities in the oxide layers little significance is attached to these various constants with the possible exception of abraded Fe oxidized in O_2.[2]

Metallographic sections through the oxide layers formed in water vapour–argon are shown in Fig. 2. (The layers formed in O_2, curves 3 and 4 of Fig. 1, are like those of Fig. 4 in ref. 2.) All four specimens show two oxide phases differing in reflectivity and identified by X-ray diffraction as Fe_2O_3 and Fe_3O_4. The Fe_2O_3 on the specimens of curves 1 and 2 may have formed at the end of the runs when they were raised quickly, still in a damp argon, to the cool end of the open furnace tube. The pores in the Fe_2O_3 needles of Fig. 2a, probably enlarged during polishing, would then reflect the volume decrease when Fe_3O_4 (density 5·18) converts to Fe_2O_3 (density 5·24).

Figure 2a does not show the gap between oxide and metal which would be predicted if the stifling of oxidation of curve 1 relative to curve 2 was due to pore formation. There are two possible causes: a gap is present but is very small because of the slow oxidation rate, or has been obscured by smearing of the surface during polishing of the taper section; or a gap was formed initially but, as the flow of vacancies slowed, collapsed by plastic deformation of oxide under the differential pressure of 1 atm. This latter phenomenon has been observed with annealed ultrapure Fe in O_2.

Thus the effect of cold work in increasing the oxidation of Fe to Fe_3O_4 is evident in the three atmospheres, O_2, CO_2 and water vapour, although it has still to be established that in each case the explanation is that cold-worked metal supplies vacancy

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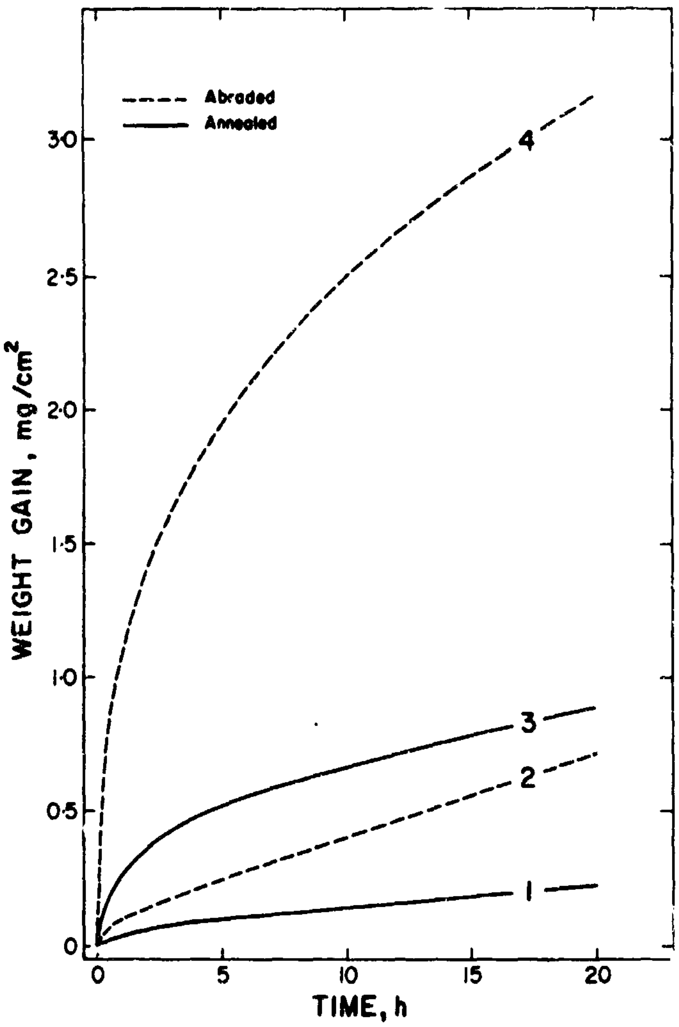

FIG. 1. Oxidation curves of annealed and abraded Fe in water vapour-argon (curves 1 and 2) and in O_2 (curves 3 and 4) at 550°C for 20 h.

sinks to suppress pore formation. The enhanced local oxidation at metal grain boundaries seen in Fig. 2a lends support to the mechanism in the case of water vapour since it is reasonable that vacancies would be readily annihilated at grain boundaries. In some work in progress we have observed a related effect in annealed Fe–C alloys oxidized in O_2: the oxide is thick locally over pearlite islands presumably because the interlamellar phase boundaries act as vacancy sinks. It will be of interest to see the shape of the oxidation curves and the scale structure of Dr. Price's Fe–Co_2 experiments when they are published.

As to the comments of Dr. Price on the kinetics of the earlier paper,[2] we agree that because of the complexity of the oxidation process, the values of the rate constants and activation energies are of little fundamental significance. We do not agree, however, with his speculations regarding recrystallization since these are not consistent with our experimental results—i.e. if faster recrystallization at temperatures approaching 600°C were to cause cold-worked and annealed Fe to oxidize at similar rates, separated oxide (and a similar oxidation curve) should be observed on both the annealed and cold-worked specimens, which is not the case (Figs. 2–5, ref. 2). As a result it is still our opinion that below 600°C greater reliance can be placed on rate constants obtained from cold-worked Fe. Again, if rapid recrystallization were the

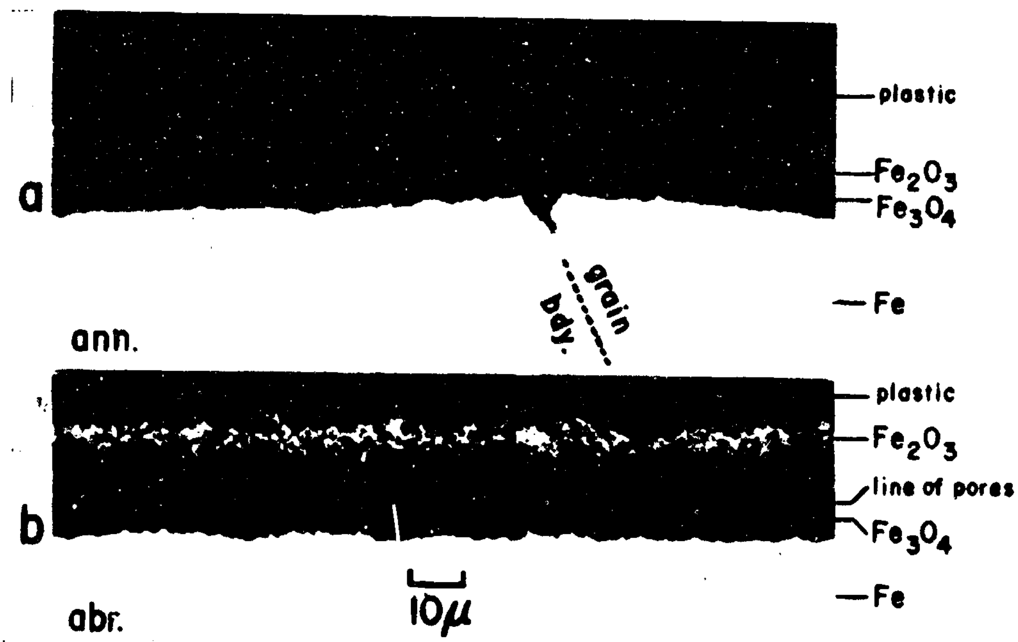

FIG. 2. Metallographic taper sections through oxide layers formed in water vapour-argon on annealed and abraded Fe in 20 h at 550°C. (a) Curve 1, annealed; taper ratio 7 : 1. (b) Curve 2, abraded; taper ratio 4 : 1. Unetched, × 750.

In (a) white needles of Fe_2O_3 contain holes (black) which may be partly artifact. The ridge on the oxide surface and the associated trench in the metal occur at metal grain boundary. In (b) oxide ridges do not occur opposite metal grain boundaries. In (a) and (b) the authenticity of the oxide–metal interface is in doubt. In (b) the line of pores (black dots) in Fe_3O_4 layer one-third out from metal surface is real and constitutes a plane of weakness at which the oxide sometimes splits.

cause of the similar oxidation behaviour of abraded and annealed Fe at temperatures high enough for FeO to form, both should show separated oxide whereas neither does (Fig. 7 in ref. 2). Our own speculation to account for the higher apparent activation energy with annealed Fe would be simply that, due to increased oxide plasticity, an increase in temperature would promote re-establishment of contact by squashing of the separated oxide on to the metal, hence a faster increase with temperature of apparent rate constant for annealed than cold-worked Fe.

Very conveniently the oxidation of Fe to Fe_3O_4 appears to be especially sensitive to several experimental variables and with further investigation may be made to yield considerable information on oxidation mechanisms. In our laboratory the work is being extended to observe the effect of pressure and composition of the oxidizing gas, including abrupt pressure changes during a run; effect of impurities and inclusions in the Fe on oxide porosity and how the porosity changes with time; effect of cold work on the oxidation of a series of Fe–C alloys; and the effect of prior oxide and the procedure for first exposing the metal to the gas. Other attractive projects are high-pressure studies, tracer experiments and some method of observing pores as they form, such as by hot-stage microscopy, but these still are in the planning stage.

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